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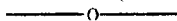
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IRON ORES OF OHIO AND THEIR TREATMENT.

BY EMERSON MC MILLEN.

While the title of this paper indicates subjects of great economic importance, there really exists no good reasons why a specially prepared paper on these subjects should be presented to the society.

All our members have, or can have access to chapters five and six of the fifth volume of Ohio Geology. In those chapters the subjects are discussed ably and at length, by Dr. Edward Orton, Chief Geologist, and Prof. N. W. Lord, chemist to the survey; were the chapters not so

long, I should read them to the Institute, in lieu of this paper.

When requested to discuss these subjects, I agreed to do so, chiefly because I thought I could do it with less expenditure of time and labor, than I could discuss other subjects that were to be brought before the Institute.

I had in my mind a paper which I read before another society in 1876, which I thought would require but little change to adapt it to the requirements of this meeting.

In this, however, I was mistaken to a large degree.

My experience in the use of Ohio ores being confined exclusively to those of the Hanging Rock region, must be my excuse for so often referring to the ores of that locality. However, the remarks will generally apply to the entire iron region of the State, as the ores of this geological horizon extend nearly the whole length of the State, from North to South along a line near the eastern border.

The genesis and deposit of iron ores are subjects of great interest, too vast to be touched upon in this paper, even were I competent to discuss them. I may add, however, that the ore beds of Ohio or such as are worked, are regarded as sedimentary deposits. Having before existed in many forms, dissolved in water as ferrous oxide, oxydized to ferric oxide, and deposited in the water as either brown ore or as limonites.

I have seen no theory advanced as to how so much of the ore became carbonates. I will suggest the idea that under proper conditions the oxides—most probably the protoxide—combines with the carbonic acid escaping from decayed vegetation, and also from the calcareous formations, which on becoming insoluble—passing from a bicarbonate to a carbonate—gives off a molecule of carbonic acid.

That those unfamiliar with the various forms of ore may the more readily comprehend what follows, I will briefly notice iron ores in general. Many forms of iron ore exist, many specimens of the same name being chemically different, and many forms chemically about

the same, being very different in structure and general appearance.

As a rule, the older and the more crystalline the ore, the purer it is. The magnetic is the richest in iron of any of the oxides. The sesquioxide follows, and the carbonate is lowest in the scale. This graduation is based on the idea that there really exists no definite chemical compound such as might be classed a "limonite."

Magnetic oxide has a specific gravity 4.9 to 5.2. Color usually being black streak; when pure, black. This ore is composed of 31.03 per cent. of Fe_2O_3 + 68.97 per cent. of $\text{Fe}_2\text{O}_3 = 72.4$ iron + 27.6 oxygen. It is usually written Fe_3O_4 . Frequently one portion of the ferrous oxide is replaced by magnesia or titanate. We have none of this ore in working quantity in Ohio.

The celebrated Swedish irons are made from magnetic ores. The hematites are numerous. The formula of red hematite is Fe_2O_3 + 70 per cent. iron plus 30 oxygen. Brown hematite has same composition, plus water. "Brown" ore and limonite are species of the hematite class. Just what constitutes a "brown hematite" and what limonite proper, would be difficult to determine. But usually authorities will call the ore brown hematite that has the least water in it, and the ores with most water in combination, limonite.

Most writers put Fe_2O_3 at 85.6 to 14.4 of H_2O , for the relative proportions of oxide of iron and water in limonites, but others have classed ores as limonites that have but 5 per cent. of combined water. From studying the analyses of these ores made by others, and from my own

observation in analyzing ores of the Hanging Rock region, I am not satisfied that there is any point of hydration where we can well draw the line between the "brown hematite" and the limonite. The difference is only in degree and not in kind.

The formula for limonite, based on the proportions given above is $2\text{Fe}_{\frac{2}{3}}\text{O}_{\frac{2}{3}} + 3\text{H}_{\frac{2}{3}}\text{O}$. The color, structure, etc., you are all quite familiar with.

The "bog ores" belong to the brown hematite and limonite classes, and the descriptions of many of these correspond exactly with our gray ores, so far as the structure is concerned, but not as to color. The "olitic ores" are described as looking like an aggregation of fish eggs.

The calcareous and argillaceous carbonates, or what we call our blue and gray limestone ores, are found in the coal measures, and are often impregnated with carbonate of calcium, to that degree that we are in doubt whether to call it a calcareous iron ore, or a ferruginous. The color runs from gray to grayish blue, brown and bluish black and slate color, and in Lawrence county some 20 feet below the ferri-ferous limestone, there exists a thin vein of lemon colored carbonate of iron, known as "canary" ore, some samples of which when calcined have yielded as high as 58 per cent. of iron.

The "black band" ores are proto-carbonates mixed with a large per cent. of bituminous matter. Its formula would be FeO , $\text{CO}_{\frac{2}{3}}$ or $\text{FeO}_{\frac{2}{3}}\text{C}$, that is O 62.07 per cent. plus $\text{C O}_{\frac{2}{3}}$, 37.93 per cent. or to reduce still further iron 48.28, plus oxygen 41.38, plus carbon 10.34 = 100; of course this is the pure carbonate without the bituminous matter.

The ores of Ohio are chiefly carbonates and limonites. In the Hanging Rock region, the chief ores are the "red limestone," "blue limestone" and "gray limestone." The first of these would generally be called a limonite, though sometimes it is more properly a brown hematite; the second a carbonate and the third a mixture of these two, in some localities called the gray ironstone.

It is generally believed by the iron men of the Hanging Rock region, that the gray ore is simply the blue carbonate in a transition period or condition, changing to the red limonite; and they attempt to point out the conditions essential to this change—that is the limestone must have seams or cracks to drain the water away, and the ground must be either lightly distributed over the ore, or very porous, and that the change can not occur in wet close land and about the heads of ravines where exposure do not occur. This, to say the least, is a convenient sort of theory, but the facts do not bear it out. In the first place, the blue ore is usually a hard compact mass, while the gray is to the eye an aggregation of small rounded particles. The change, if it occurred, should increase the per cent. of iron in the gray ore, while in fact the gray ore has a smaller per cent. of iron than the blue. Again, the change should permit a portion of the silicious matter to be washed out, while in fact the gray ore has about double the quantity of silicious matter that the blue ore contains. Again, the blue is held together in a mass by cementation as it were, while much of the gray ore is held together by a matrix of

potter's clay. These facts I deem sufficient to disprove the claim that gray ore is the blue changing to red.

The "block ores" of the Hanging Rock region are brown hematites usually a core of carbonite of iron. There are many ores throughout the State that in appearance, look like the Hanging Rock ones, and doubtless are, geologically, the same, yet in most localities they lack the richness of, or contain so much phosphorus that they are not so valuable as the ore of that locality.

The average analysis of nine samples of the Hocking Valley ores, made in 1869 when the fever of that region was becoming contagious, shows metallic iron 31.37 per cent., while the silicious matter is 25.08 per cent., and many of the ores that were then promising in appearance and in quality, have on further investigation proven worthless in quality, or been cut out by the sand stone in going further into the hills.

The following is the analysis of a sample from the great Bessemer vein of the Hocking Iron District about which much was said and written a few years ago:

Combibed water,	8.90
Metallic iron,	41.31
Phosphate of Al.,59
Phosphate of Mag.,70
Silicious matter,	25.60
Alumina,	1.56
Phosphate Lime,	1.10
Oxide Manganese,	2.15

I believe this seam is not worked. A sample of ore from Vesuvius furnace lands in Lawrence county, analyzed by Wormley, gave 54.39 per cent. of metallic iron, and but 2 per cent. of silicious matter. One

ton of this ore is worth three of the Bessemer ore.

The average of a great number of samples of the different Hanging Rock ores show up as follows:

	Red	Blue	Gray
Iron	51.66	38.05	35.52
Silicious matter 2.	13.00	20.	
Phosphorus64	.89	.11

You will observe that the averages show the blue ore richer in iron and much lower in silicious matter than the gray.

The average of fifty samples of the Hanging Rock ores analyzed by the writer, gave an average of about 45 per cent. of iron for red, for blue about 42 per cent. (this included several samples of Canary ore, which was above the average) and for gray about 35 per cent. of metallic iron.

TREATMENT.

The only advantage to be gained by roasting either the Magnetic, Specular, or Red Hematite ore is the oxidation of the pyrites, and hydration (if I may use that word in this connection) of the phosphoric acid. But not so with the brown Hematites, Limonites and Carbonates.

By calcining the brown ores and Limonites, a large per cent. of water is driven off. and at a less expense of fuel in the kiln than could be done in the blast furnace. The pyrites are oxidized and the freed sulphur either passes off as sulphurous acid or as sulphides converted into soluble sulphates and is washed away by the rains. This is supposing of course that the ore is roasted in open kilns. Another advantage to be gained in roasting these ores, is in making it possible to screen or separate the dirt from the ore.

In Ohio the coal measures are associated with a fire or potter's clay, which during the wet season and wet days sticks to the ore and can only be separated by washing or roasting and screening.

Probably the better way to treat all Carbonates and Limonites would be to burn them in such manner that the ore in the kiln could be saturated with steam while hot, and then flooded with water, not only thereby washing out the sublimed sulphur, sulphurous acids and soluble sulphates, but by decomposition of steam, drive off phosphorus as phosphoretted hydrogen. The carbonates are more improved by roasting than any other class of ores. It occurs to the writer that it would be almost impossible to economically make a good article of pig from carbonates without roasting.

Previous to calcination the formula is Fe O plus CO_2 . After calcination the formula is Fe_2O_3 . Supposing that the ore was a pure carbonate, the loss in weight would be per ton of 2,268 pounds, 492.6

pounds; the loss represented by 258.1 lbs.; or 11.38 % oxygen, and 234.51 pounds or 10.34 per cent. carbon; total 21.72 per cent.

It is unquestionably essential to the economical working of a blast furnace that this chemical change should occur before the ore is charged, for the reason as before stated, the carbonic acid can be driven off by the calcining process with fuel of an inferior quality and consequently at less cost than can be done in a blast furnace, and again, the ore is rendered porous by calcining, thereby permitting the reduced gases to permeate the ore and hasten reduction, or in other words reduction will begin at a point higher up in the furnace. But the greatest gain is this, that the reduction being hastened the ore is thoroughly reduced before it reaches a point in the furnace where the temperature is sufficient to melt protoxide of iron, in which form much of the ore will pass, in the form of slag from the furnace if reduction is largely consummated before the mass is melted.
